ORIGINAL

Application Based on

Docket **87152AEK**
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ORGANIC ELEMENT FOR ELECTROLUMINESCENT DEVICES

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Express Mail Label No.: EV293530176US

Date: March 26, 2004

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ORGANIC ELEMENT FOR ELECTROLUMINESCENT DEVICES

FIELD OF INVENTION

This invention relates to organic electroluminescent devices. More specifically, this invention relates to devices that emit light from a current-conducting organic layer and have high luminance and good stability.

BACKGROUND OF THE INVENTION

While organic electroluminescent (EL) devices have been known for over two decades, their performance limitations have represented a barrier to many desirable applications. In simplest form, an organic EL device is comprised of an anode for hole injection, a cathode for electron injection, and an organic medium sandwiched between these electrodes to support charge recombination that yields emission of light. These devices are also commonly referred to as organic light-emitting diodes, or OLEDs. Representative of earlier organic EL devices are Gurnee et al. US 3,172,862, issued Mar. 9, 1965; Gurnee US 3,173,050, issued Mar. 9, 1965; Dresner, "Double Injection Electroluminescence in Anthracene", *RCA Review*, **30**, 322-334, (1969); and Dresner US 3,710,167, issued Jan. 9, 1973. The organic layers in these devices, usually composed of a polycyclic aromatic hydrocarbon, were very thick (much greater than 1 μm). Consequently, operating voltages were very high, often greater than 100V.

More recent organic EL devices include an organic EL element consisting of extremely thin layers (e.g., less than 1.0 μm) between the anode and the cathode. Herein, the term "organic EL element" encompasses the layers between the anode and cathode. Reducing the thickness lowered the resistance of the organic layer and has enabled devices that operate at much lower voltage. In a basic two-layer EL device structure, described first in US 4,356,429, one organic layer of the EL element adjacent to the anode is specifically chosen to transport holes, and therefore, it is referred to as the hole-transporting layer, and the other organic layer is specifically chosen to transport electrons, and is referred to as the electron-transporting layer. Recombination of the injected holes and electrons within the organic EL element results in efficient electroluminescence.

There have also been proposed three-layer organic EL devices that contain an organic light-emitting layer (LEL) between the hole-transporting layer and electron-transporting layer, such as that disclosed by Tang et al (*J. Appl. Phys.*, **65**, Pages 3610-3616, (1989)). The light-emitting layer commonly consists of a host material doped with a guest material, also known as a dopant. Still further, there has been proposed in US 4,769,292 a four-layer EL element comprising a hole-injecting layer (HIL), a hole-transporting layer (HTL), a light-emitting layer (LEL) and an electron transport/injection layer (ETL). These structures have resulted in improved device efficiency

Since these early inventions, further improvements in device materials have resulted in improved performance in attributes such as color, stability, luminance efficiency and manufacturability, e.g., as disclosed in US 5,061,569, US 5,409,783, US 5,554,450, US 5,593,788, US 5,683,823, US 5,908,581, US 5,928,802, US 6,020,078, and US 6,208,077, amongst others.

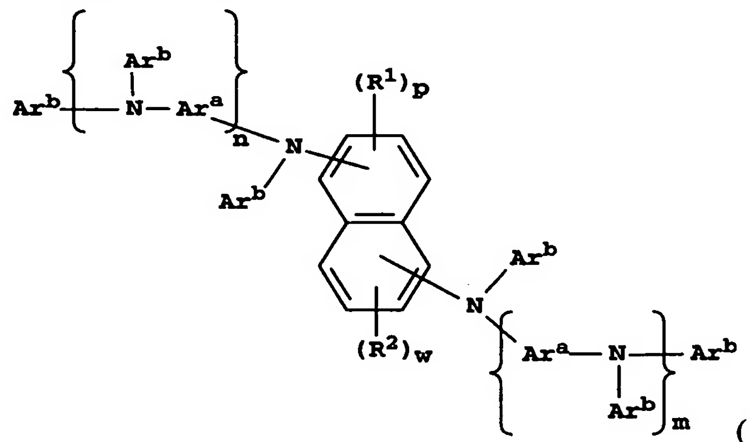
EP891121A1 and EP1029909A1 suggest the use of phenylenediamine derivatives to improve hole injecting and/or transporting properties. EP 924192A1B1, US 5759444, US 20020168543, JP 11176574A, JP 11185965A, JP 11219787A, JP 11273860A, T. Selby and S. Blackstock, *J. Am. Chem. Soc.*, **121**, 7152 (1999), and Y. Qiu, J. Qiao, Y. Gao, D. Zhang, L. Wang, Syn. Met., 129, 25 (2002) suggest the use of naphthyldiamine derivatives in EL elements generally. Many of these materials contain 1,4-diamines, which can cause the materials to have low oxidation potentials and in some cases to be thermally unstable.

US 2003/0129449A1 describes naphthylamine hole-transporting materials, which give increased luminance when used in an electroluminescent device. However, is some cases these materials can give unacceptable stability. That is, the operating lifetimes of devices using these materials may be shorter than desirable.

There remains a need for organic EL device components that will provide a desired high luminance and long operating lifetimes.

SUMMARY OF THE INVENTION

The invention provides an electroluminescent device comprising a layer containing a naphthalene compound represented by Formula (1),



(1)

wherein:

each R^1 and R^2 represents an independently selected substituent provided that adjacent substituents may join to form a ring;

p and w independently are 0-3;

the amine nitrogens on the naphthalene nucleus are located on separate rings;

m and n independently are 0, 1 or 2;

each Ar^b represents an independently selected aromatic group; and each Ar^a represents an independently selected phenylene, biphenylene or naphthalene group;

provided that at least one R_1 or R_2 substituent of the naphthalene compound represented by Formula (1) is a sterically bulky substituent.

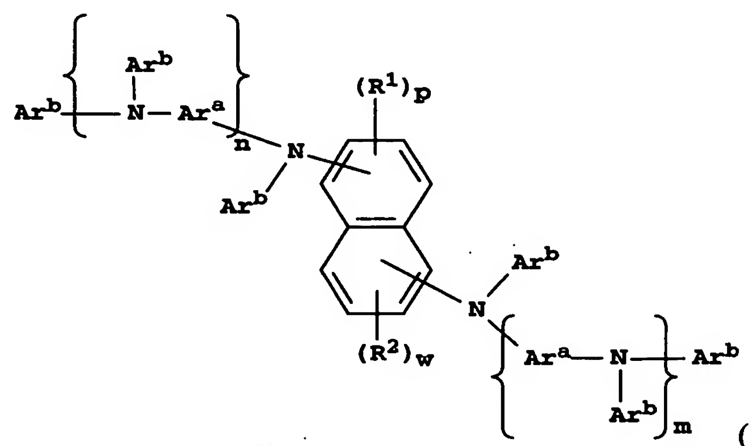
The invention also provides a display and area lighting device incorporating the device and a process for emitting light employing the device. Embodiments of the invention provide a desired high luminance and long operating lifetimes

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a cross-section of a typical OLED device in which this invention may be used.

DETAILED DESCRIPTION OF THE INVENTION

The invention comprises a multilayer electroluminescent device comprising a cathode, an anode, a light emitting layer (LEL) and a layer disposed between the cathode and anode containing a naphthalene compound. In one desirable embodiment the naphthalene compound is represented by Formula (1).



(1)

In Formula (1) the amino groups, as depicted in the formula, are on different rings of the naphthalene nucleus. In Formula (1), each R^1 and R^2 represents an independently selected substituent provided that adjacent substituents may join to form a ring. For example, R^1 and R^2 may represent phenyl groups or methyl groups. In Formula (1), p and w independently are 0-3 and m and n independently are 0, 1, or 2. Each Ar^a represents an independently selected phenylene, biphenylene or naphthalene group. Each Ar^b represents an independently selected aromatic group, such as a phenyl, tolyl, or naphthyl group. At least one substituent of the naphthalene compound represented by Formula 1 is a sterically bulky group.

A "sterically bulky" substituent as used herein means a substituent that has a Sterimol B1 value of 1.6 angstroms or greater. This value is desirable in

that it may prevent or limit exciplex formation. Thus it may inhibit the formation of excited state complexes involving one or more compounds of Formula (1) or complexes between materials of Formula (1) and other materials. In some cases the formation of exciplexes is undesirable and can shorten the operating lifetime of a device.

The Sterimol parameters for a substituent group are defined in Hansch and Leo (C. Hansch and A. Leo, *Exploring QSAR Fundamentals and Applications in Chemistry and Biology,* American Chemical Society (1995)). Values for the B_1 Sterimol parameter may be taken from Hansch, Leo and Hoekman (C. Hansch, A. Leo, and D. Hoekman, *Exploring QSAR Hydrophobic, Electronic and Steric Constant,* American Chemical Society (1995)), or if not available in those tables, Sterimol parameters can be computed with the commercially available program, TSAR version 3.3 (Accelrys Inc., San Diego, CA). Examples of substituents and their B_1 parameter values are listed in Table A

Table A

R_1	B_1 (angstroms)
CH_3	1.52
C_2H_5	1.52
i-C_4H_9	1.52
C_6H_5	1.70
c-C_6H_{11}	2.04
$CH(C_2H_5)_2$	2.11
t-C_4H_9	2.59
s-C_4H_9	2.59
$C(C_2H_5)_2C_6H_5$	3.10
mesityl	1.93
2,6-dimethylphenyl	1.86
o-tolyl	1.67

Suitably the compound of Formula (1) contains at least one R^1 or R^2 substituent that has a Sterimol B_1 value of 1.8 angstroms or greater. Desirably, at least one such substituent has a Sterimol B_1 value of 2.0 angstroms or greater. Desirably at least one of R^1 and one of R^2 in Formula (1) are present and

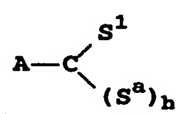
independently represent a bulky substituent that has a Sterimol B_1 value of at least 1.8 and desirably at least 2.0 angstroms or greater.

In one embodiment of the invention, a sterically bulky substituent is a branched hydrocarbon. That is, the carbon attached to the naphthyl compound is secondary or tertiary, for example, as in the case of an *s*-propyl group or *t*-butyl group. Desirably, the carbon attached to the naphthyl compound is a tertiary carbon, such as in a *t*-butyl group.

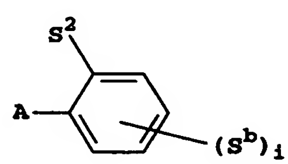
In another suitable embodiment, the sterically bulky group is an aryl group with at least one substituent on the aryl group that is adjacent to the point of attachment, for example a mesityl group or an *o*-tolyl group. In this case, desirably, the substituent on the aryl group that is adjacent to the point of attachment is not part of a fused ring.

Suitably one of R^1 and one of R^2 in Formula (1) are present and represent a sterically bulky substituent such as an independently selected branched hydrocarbon or an aryl group with at least one substituent on the aryl group that is adjacent to the point of attachment.

In one embodiment of the invention, a sterically bulky substituent is one that is represented by Formula 2a or 2b.



(2a)



(2b)

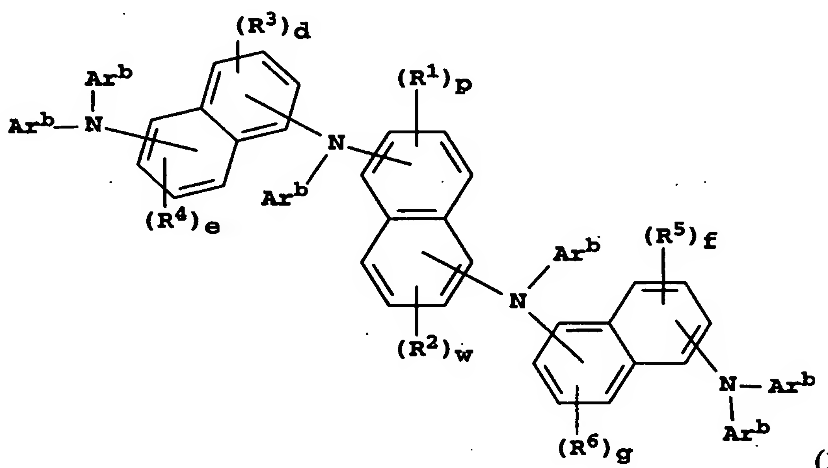
In Formula (2a) and (2b), A represents the point of attachment to Formula (1). Each S^1, S^2, S^a, and S^b independently represents a substituent, such as methyl group or phenyl group. S^1 and S^a may combine to form a saturated ring, such as a cyclohexyl ring group. In Formula (2a), h is 1 or 2, thus the carbon attached to Formula (1) has at least two substituents. In Formula (2b) i is 0-4; thus

the phenyl ring group has at least one substituent adjacent to the point of attachment. In one desirable embodiment, h is 2. Suitably S^1 and S^a, in one embodiment, represent independently selected methyl groups. In one desirable embodiment, i is 1 or greater. Suitably S^2 and S^b, in one embodiment, represent independently selected methyl groups.

Suitably at least one of R^1 in Formula (1) is represented by the bulky substituent of Formula (2a) or (2b). Desirably at least one of R^1 and one of R^2 in Formula (1) are independently represented by Formula (2a) or (2b).

In another suitable embodiment, Ar^a represents an independently selected naphthalene group, such as a 1,5-diaminonaphthalene group, a 2,6-diaminonaphthalene group or a 2,7-diaminonaphthalene group. Suitably Ar^a is substituted with a sterically bulky substituent.

In one desirable embodiment the naphthalene compound of the invention is represented by Formula (3).

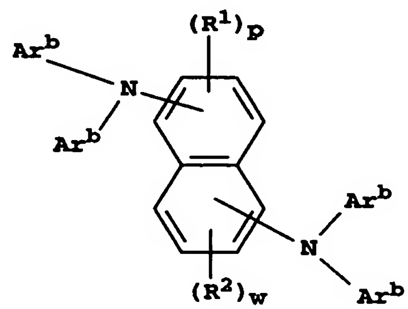


(3)

In Formula (3), Ar^b, R^1, R^2, p, and w were defined previously. R^3-R^6 each represents an independently selected substituent provided that adjacent substituents may join to form a ring. For example, R^3-R^6 may represent phenyl groups or methyl groups. In Formula (3), d, e, f, g, independently represent 0-3. Suitably at least one of R^1-R^6 is present in Formula (3) and is represented by the bulky substituent of Formula (2a) or (2b). Suitably at least two of R^1-R^6 in

Formula (3) are present and represented by the bulky substituent of Formula (2a) or (2b). Desirably at least one of R^1 and one of R^2 in Formula (1) are independently represented by Formula (2a) or (2b).

In one suitable embodiment the naphthalene compound of the invention is represented by Formula (4).



(4)

In Formula (4), Ar^b, R^1, R^2, p, and w were defined previously. Suitably at least one of R^1 is present in Formula (4) and is represented by the bulky substituent of Formula (2a) or (2b). Suitably at least one of R^1 and one of R^2 in Formula (1) is present and is represented by an independently selected bulky substituent of Formula (2a) or (2b).

The compound of Formula (1) is usually contained in a layer between the anode and the LEL. That layer may or may not be adjacent to the anode. In some embodiments of the invention, it is desirable that the compound is not adjacent to the LEL and there is present in a layer between the anode and LEL a second compound that functions to improve hole transporting.

Unless otherwise specifically stated, use of the term "substituted" or "substituent" means any group or atom other than hydrogen. Additionally, when the term "group" is used, it means that when a substituent group contains a substitutable hydrogen, it is also intended to encompass not only the substituent's unsubstituted form, but also its form further substituted with any substituent group or groups as herein mentioned, so long as the substituent does not destroy properties necessary for device utility. Suitably, a substituent group may be halogen or may be bonded to the remainder of the molecule by an atom of carbon,

silicon, oxygen, nitrogen, phosphorous, sulfur, selenium, or boron. The substituent may be, for example, halogen, such as chloro, bromo or fluoro; nitro; hydroxyl; cyano; carboxyl; or groups which may be further substituted, such as alkyl, including straight or branched chain or cyclic alkyl, such as methyl, trifluoromethyl, ethyl, *t*-butyl, 3-(2,4-di-*t*-pentylphenoxy) propyl, and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, *sec*-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-*t*-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl, 4-*t*-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, *alpha*-(2,4-di-*t*-pentyl-phenoxy)acetamido, *alpha*-(2,4-di-*t*-pentylphenoxy)butyramido, *alpha*-(3-pentadecylphenoxy)-hexanamido, *alpha*-(4-hydroxy-3-*t*-butylphenoxy)-tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, *N*-methyltetradecanamido, *N*-succinimido, *N*-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and *N*-acetyl-*N*-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-*t*-butylphenoxycarbonylamino, phenylcarbonylamino, 2,5-(di-*t*-pentylphenyl)carbonylamino, *p*-dodecyl-phenylcarbonylamino, *p*-tolylcarbonylamino, *N*-methylureido, *N,N*-dimethylureido, *N*-methyl-*N*-dodecylureido, *N*-hexadecylureido, *N,N*-dioctadecylureido, *N,N*-dioctyl-*N'*-ethylureido, *N*-phenylureido, *N,N*-diphenylureido, *N*-phenyl-*N*-*p*-tolylureido, *N*-(m-hexadecylphenyl)ureido, *N,N*-(2,5-di-*t*-pentylphenyl)-*N'*-ethylureido, and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-tolylsulfonamido, *p*-dodecylbenzenesulfonamido, *N*-methyltetradecylsulfonamido, *N,N*-dipropyl-sulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as *N*-methylsulfamoyl, *N*-ethylsulfamoyl, *N,N*-dipropylsulfamoyl, *N*-hexadecylsulfamoyl, *N,N*-dimethylsulfamoyl, *N*-[3-(dodecyloxy)propyl]sulfamoyl, *N*-[4-(2,4-di-*t*-pentylphenoxy)butyl]sulfamoyl, *N*-methyl-*N*-tetradecylsulfamoyl, and *N*-dodecylsulfamoyl; carbamoyl, such as *N*-methylcarbamoyl, *N,N*-

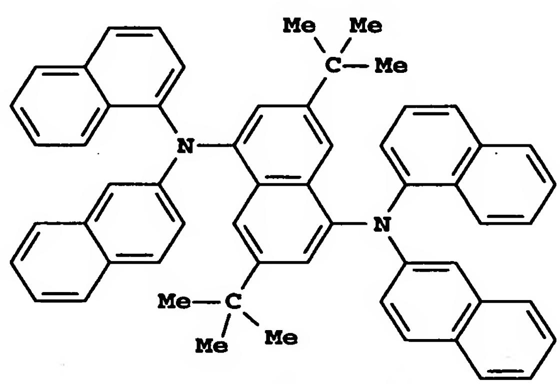
dibutylcarbamoyl, *N*-octadecylcarbamoyl, *N*-[4-(2,4-di-*t*-pentylphenoxy)butyl]carbamoyl, *N*-methyl-*N*-tetradecylcarbamoyl, and *N,N*-dioctylcarbamoyl; acyl, such as acetyl, (2,4-di-*t*-amylphenoxy)acetyl, phenoxycarbonyl, *p*-dodecyloxyphenoxycarbonyl methoxycarbonyl, butoxycarbonyl, tetradecyloxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxycarbonyl, and dodecyloxycarbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxysulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-tolylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and *p*-tolylsulfinyl; thio, such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-*t*-octylphenylthio, and *p*-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-dodecylamidobenzoyloxy, *N*-phenylcarbamoyloxy, *N*-ethylcarbamoyloxy, and cyclohexylcarbonyloxy; amine, such as phenylanilino, 2-chloroanilino, diethylamine, dodecylamine; imino, such as 1 (*N*-phenylimido)ethyl, *N*-succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be substituted and which contain a 3 to 7 membered heterocyclic ring composed of carbon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen, sulfur, phosphorous, or boron. such as 2-furyl, 2-thienyl, 2-benzimidazolyloxy or 2-benzothiazolyl; quaternary ammonium, such as triethylammonium; quaternary phosphonium, such as triphenylphosphonium; and silyloxy, such as trimethylsilyloxy.

If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired

desirable properties for a specific application and can include, for example, electron-withdrawing groups, electron-donating groups, and steric groups. When a molecule may have two or more substituents, the substituents may be joined together to form a ring such as a fused ring unless otherwise provided. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

Illustrative examples of compounds of Formula (1) useful in the present invention are the following:

Inv-1



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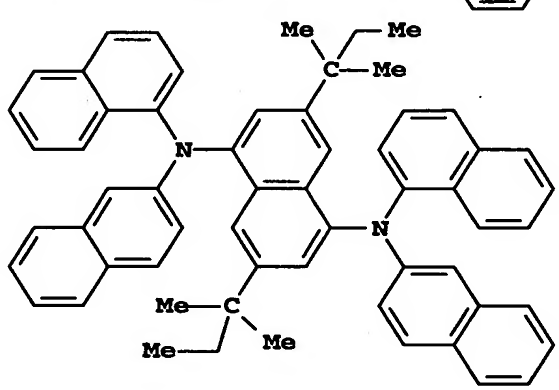

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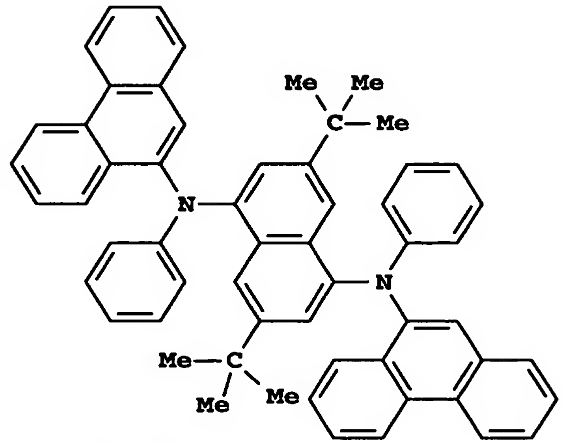

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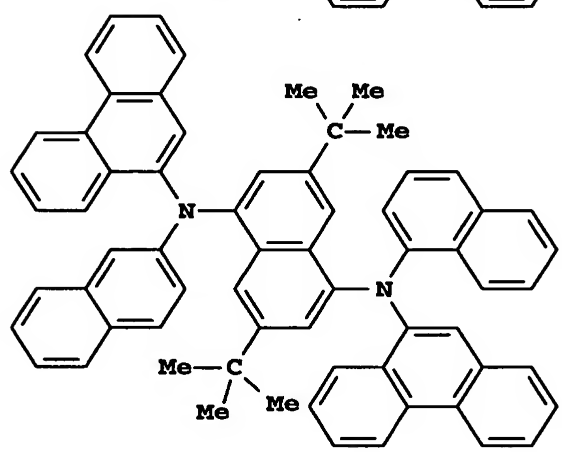

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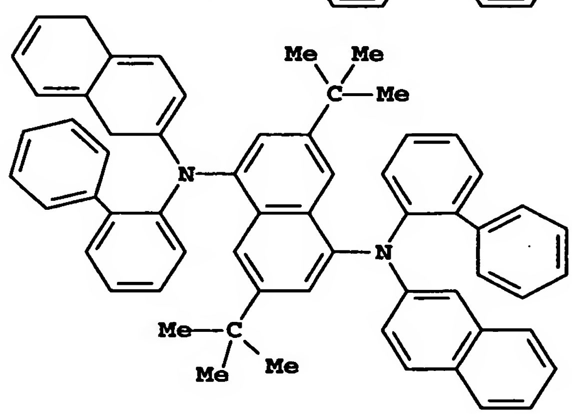

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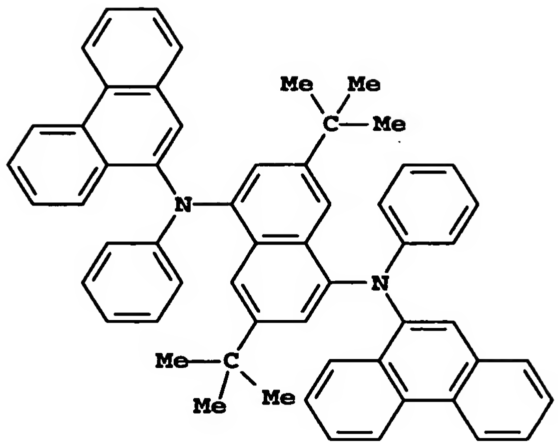

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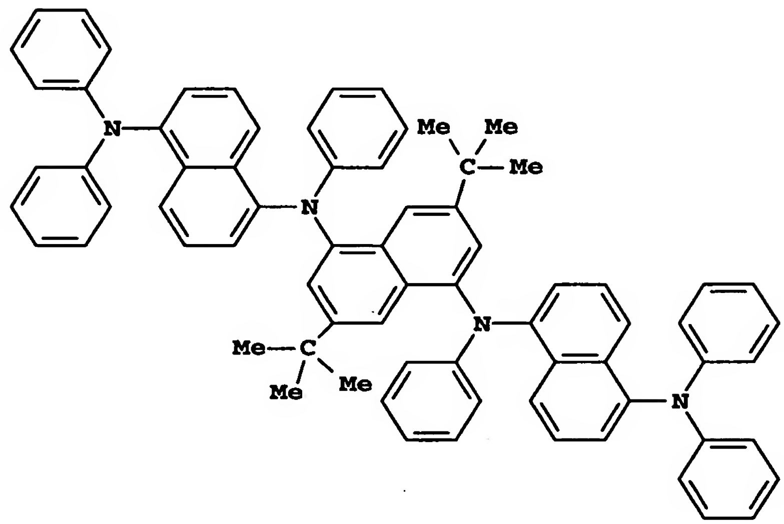

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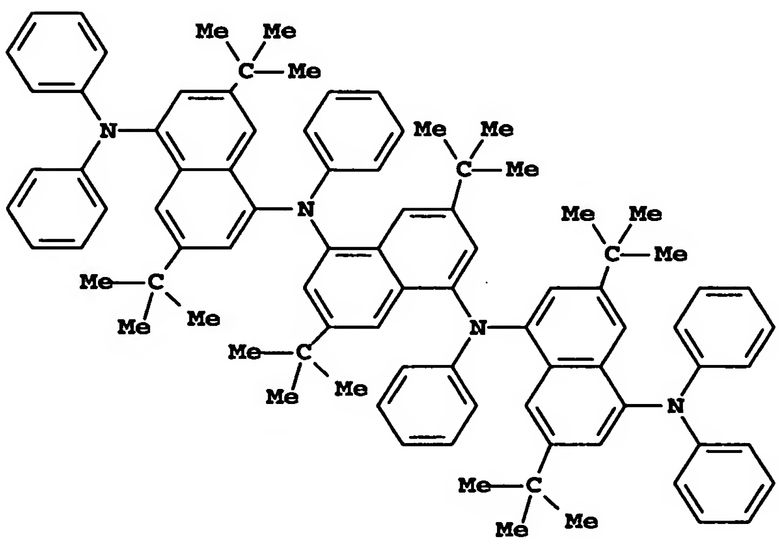

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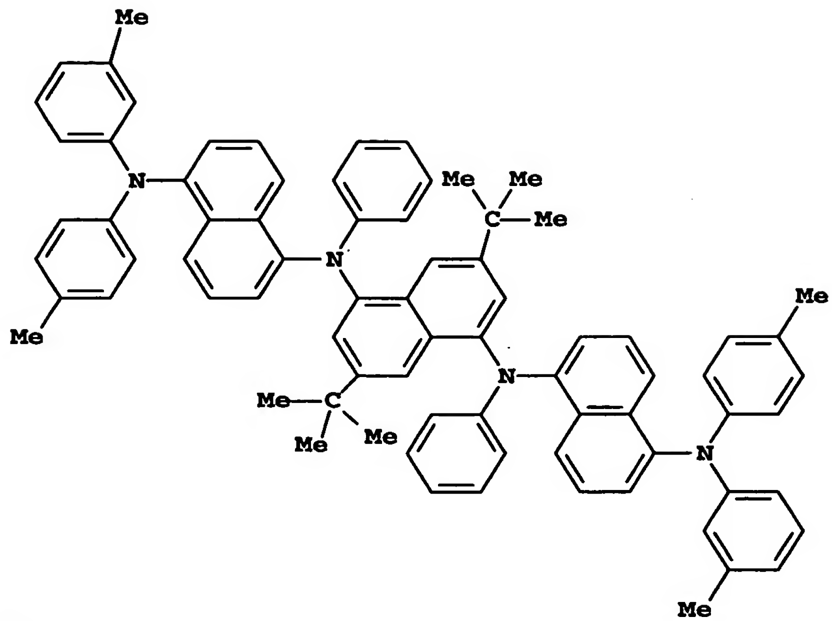

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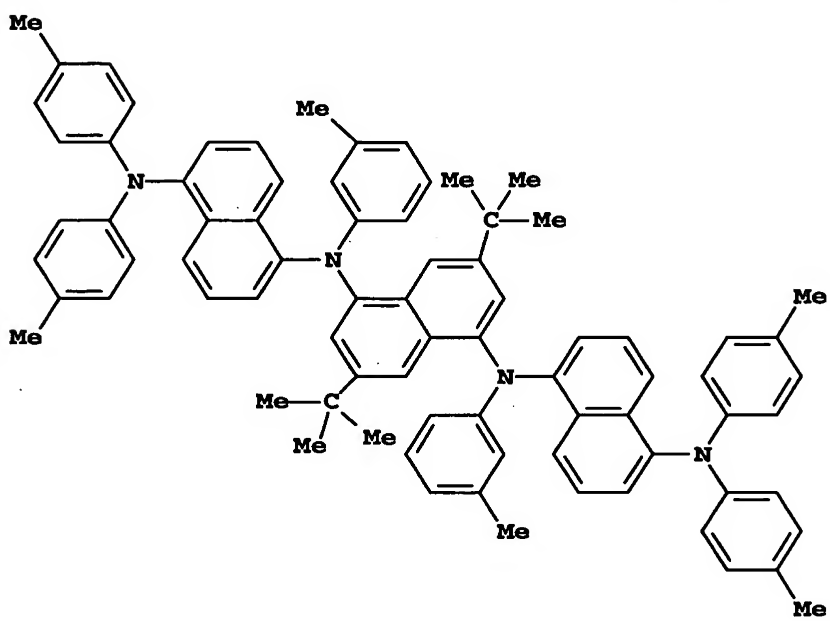

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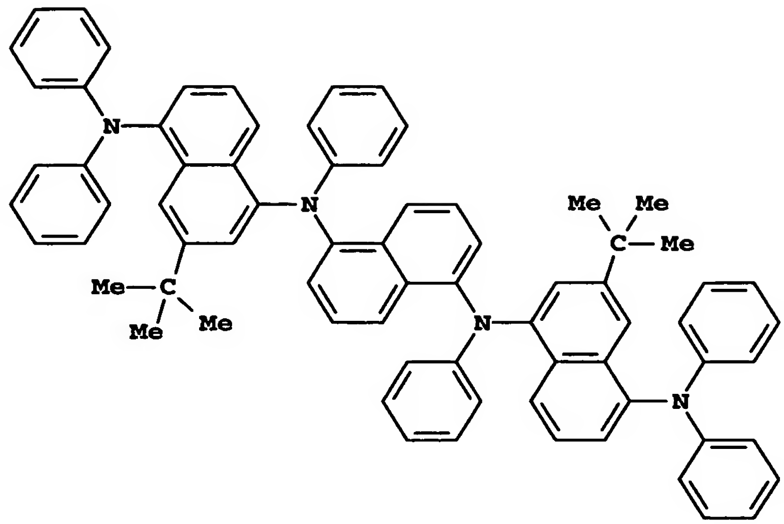

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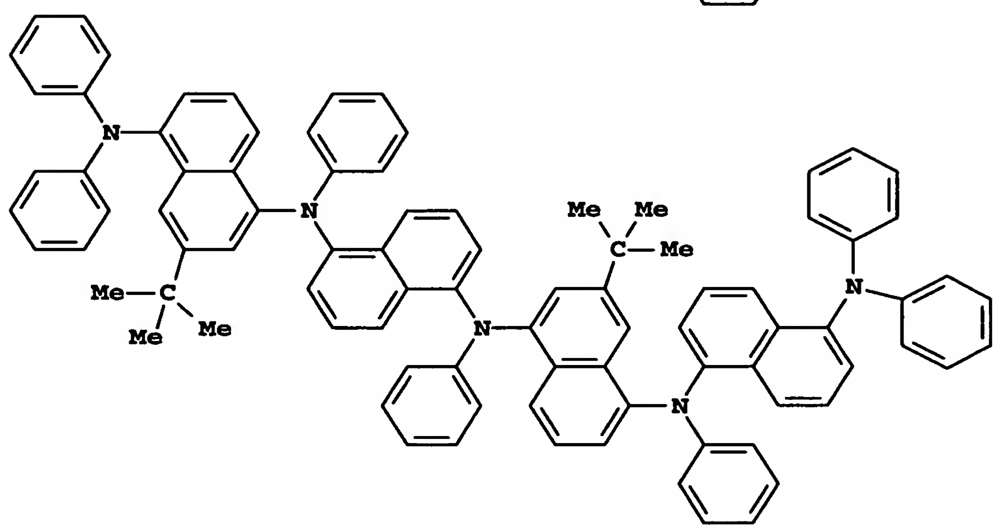

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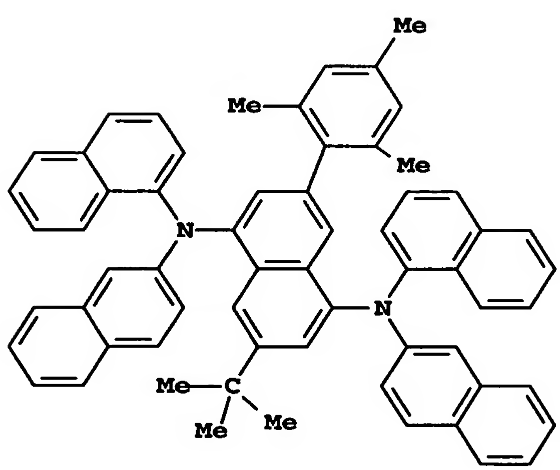

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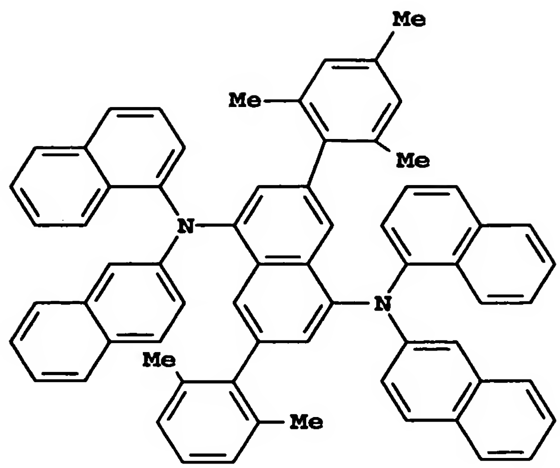

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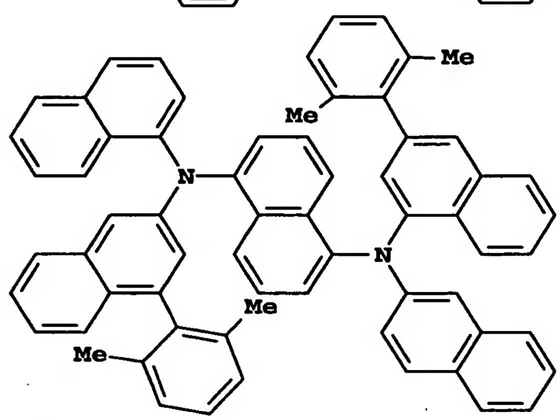

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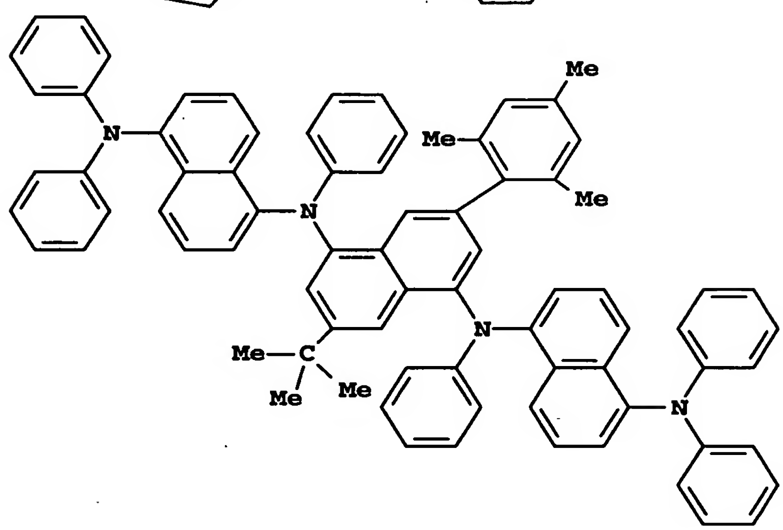

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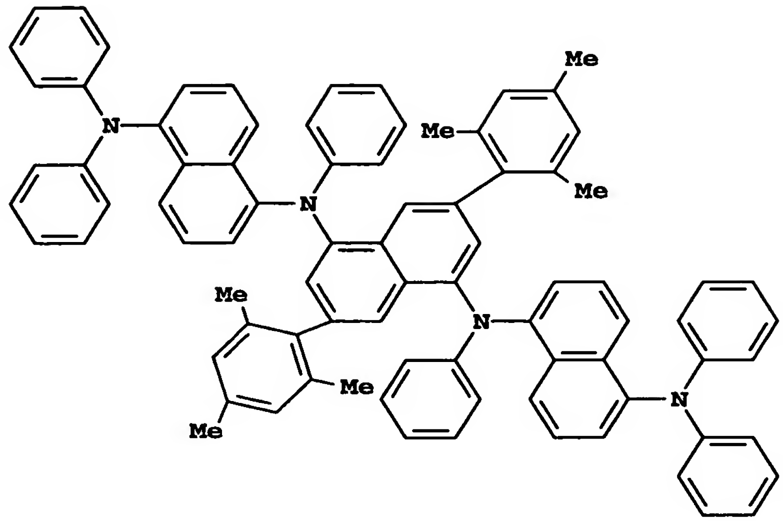

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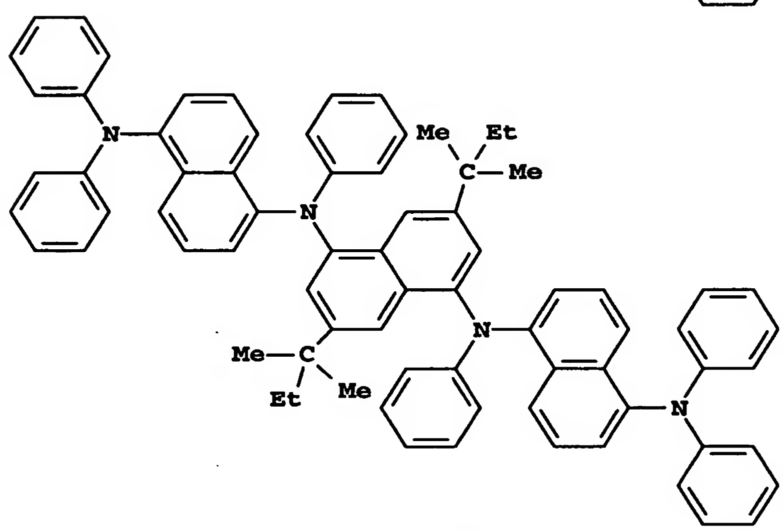

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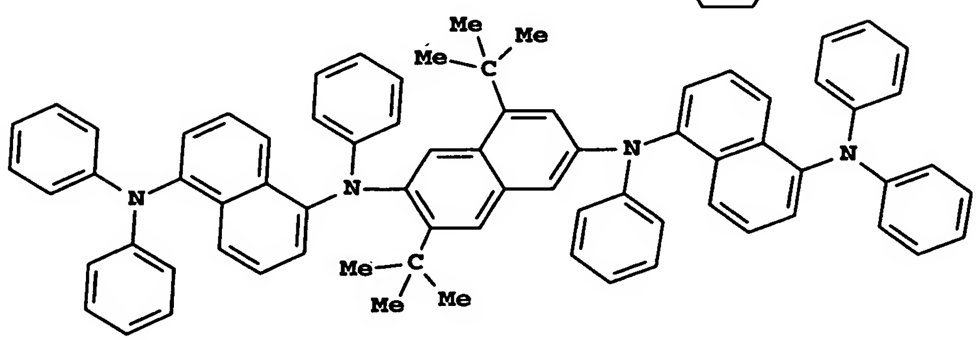

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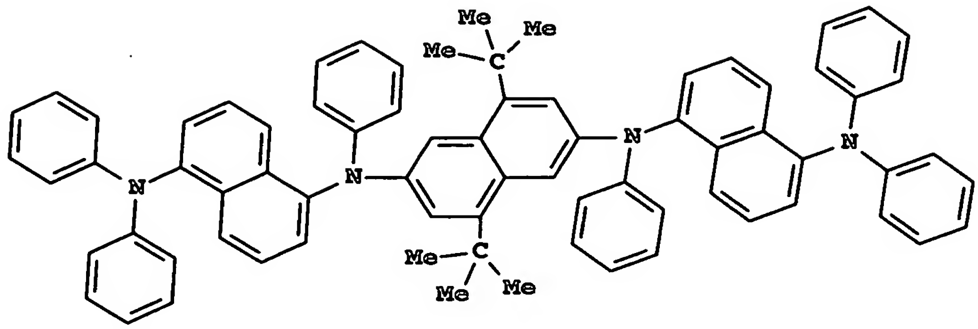

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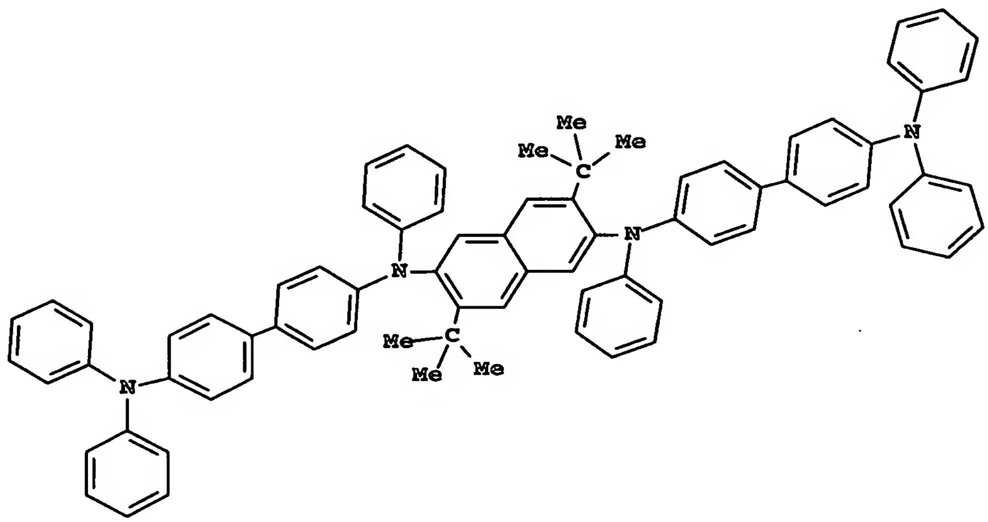

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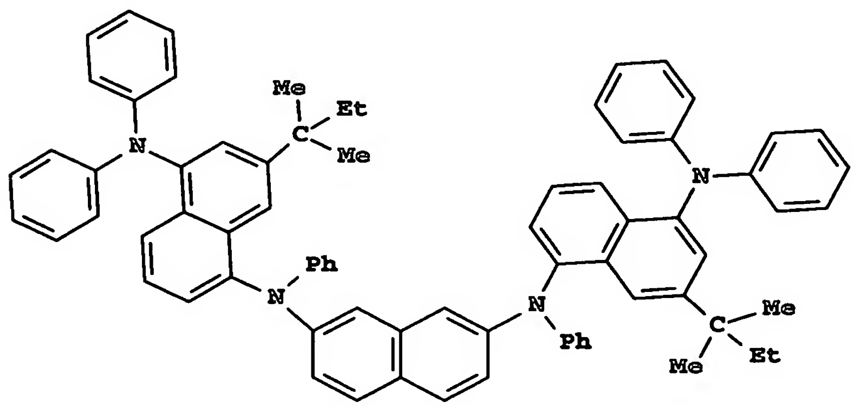

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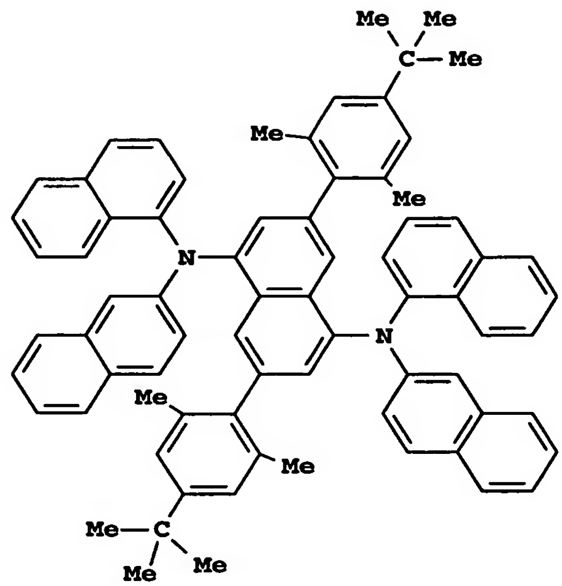


General Device Architecture

The present invention can be employed in many EL device configurations using small molecule materials, oligomeric materials, polymeric materials, or combinations thereof. These include very simple structures comprising a single anode and cathode to more complex devices, such as passive matrix displays comprised of orthogonal arrays of anodes and cathodes to form pixels, and active-matrix displays where each pixel is controlled independently, for example, with thin film transistors (TFTs).

There are numerous configurations of the organic layers wherein the present invention can be successfully practiced. The essential requirements of an OLED are an anode, a cathode, and an organic light-emitting layer located between the anode and cathode. Additional layers may be employed as more fully described hereafter.

A typical structure according to the present invention and especially useful for a small molecule device, is shown in FIG. 1 and is comprised of a substrate **101**, an anode **103**, a hole-injecting layer **105**, a hole-transporting layer **107**, a light-emitting layer **109**, an electron-transporting layer **111**, and a cathode **113**. These layers are described in detail below. Note that the substrate **101** may alternatively be located adjacent to the cathode **113**, or the substrate **101**

may actually constitute the anode **103** or cathode **113**. The organic layers between the anode **103** and cathode **113** are conveniently referred to as the organic EL element. Also, the total combined thickness of the organic layers is desirably less than 500 nm. If the device includes phosphorescent material, a hole-blocking layer, located between the light-emitting layer and the electron-transporting layer, may be present.

The anode **103** and cathode **113** of the OLED are connected to a voltage/current source through electrical conductors. The OLED is operated by applying a potential between the anode **103** and cathode **113** such that the anode **103** is at a more positive potential than the cathode **113**. Holes are injected into the organic EL element from the anode **103** and electrons are injected into the organic EL element at the cathode **113**. Enhanced device stability can sometimes be achieved when the OLED is operated in an AC mode where, for some time period in the AC cycle, the potential bias is reversed and no current flows. An example of an AC driven OLED is described in US 5,552,678.

Substrate

The OLED device of this invention is typically provided over a supporting substrate **101** where either the cathode **113** or anode **103** can be in contact with the substrate. The electrode in contact with the substrate **101** is conveniently referred to as the bottom electrode. Conventionally, the bottom electrode is the anode **103**, but this invention is not limited to that configuration. The substrate **101** can either be light transmissive or opaque, depending on the intended direction of light emission. The light transmissive property is desirable for viewing the EL emission through the substrate **101**. Transparent glass or plastic is commonly employed in such cases. The substrate **101** can be a complex structure comprising multiple layers of materials. This is typically the case for active matrix substrates wherein TFTs are provided below the OLED layers. It is still necessary that the substrate **101**, at least in the emissive pixelated areas, be comprised of largely transparent materials such as glass or polymers. For applications where the EL emission is viewed through the top electrode, the transmissive characteristic of the bottom support is immaterial, and therefore the

substrate can be light transmissive, light absorbing or light reflective. Substrates for use in this case include, but are not limited to, glass, plastic, semiconductor materials such as silicon, ceramics, and circuit board materials. Again, the substrate **101** can be a complex structure comprising multiple layers of materials such as found in active matrix TFT designs. It is necessary to provide in these device configurations a light-transparent top electrode.

Anode

When the desired electroluminescent light emission (EL) is viewed through the anode, the anode **103** should be transparent or substantially transparent to the emission of interest. Common transparent anode materials used in this invention are indium-tin oxide (ITO), indium-zinc oxide (IZO) and tin oxide, but other metal oxides can work including, but not limited to, aluminum- or indium-doped zinc oxide, magnesium-indium oxide, and nickel-tungsten oxide. In addition to these oxides, metal nitrides, such as gallium nitride, and metal selenides, such as zinc selenide, and metal sulfides, such as zinc sulfide, can be used as the anode **103**. For applications where EL emission is viewed only through the cathode **113**, the transmissive characteristics of the anode **103** are immaterial and any conductive material can be used, transparent, opaque or reflective. Example conductors for this application include, but are not limited to, gold, iridium, molybdenum, palladium, and platinum. Typical anode materials, transmissive or otherwise, have a work function of 4.1 eV or greater. Desired anode materials are commonly deposited by any suitable means such as evaporation, sputtering, chemical vapor deposition, or electrochemical means. Anodes can be patterned using well-known photolithographic processes. Optionally, anodes may be polished prior to application of other layers to reduce surface roughness so as to minimize short circuits or enhance reflectivity.

Cathode

When light emission is viewed solely through the anode **103**, the cathode **113** used in this invention can be comprised of nearly any conductive material. Desirable materials have good film-forming properties to ensure good

contact with the underlying organic layer, promote electron injection at low voltage, and have good stability. Useful cathode materials often contain a low work function metal (< 4.0 eV) or metal alloy. One useful cathode material is comprised of a Mg:Ag alloy wherein the percentage of silver is in the range of 1 to 20 %, as described in U.S. Patent No. 4,885,221. Another suitable class of cathode materials includes bilayers comprising the cathode and a thin electron-injection layer (EIL) in contact with an organic layer (e.g., an electron transporting layer (ETL)), the cathode being capped with a thicker layer of a conductive metal. Here, the EIL preferably includes a low work function metal or metal salt, and if so, the thicker capping layer does not need to have a low work function. One such cathode is comprised of a thin layer of LiF followed by a thicker layer of Al as described in U.S. Patent No. 5,677,572. An ETL material doped with an alkali metal, for example, Li-doped Alq, is another example of a useful EIL. Other useful cathode material sets include, but are not limited to, those disclosed in U.S. Patent Nos. 5,059,861, 5,059,862, and 6,140,763.

When light emission is viewed through the cathode, the cathode **113** must be transparent or nearly transparent. For such applications, metals must be thin or one must use transparent conductive oxides, or a combination of these materials. Optically transparent cathodes have been described in more detail in US 4,885,211, US 5,247,190, JP 3,234,963, US 5,703,436, US 5,608,287, US 5,837,391, US 5,677,572, US 5,776,622, US 5,776,623, US 5,714,838, US 5,969,474, US 5,739,545, US 5,981,306, US 6,137,223, US 6,140,763, US 6,172,459, EP 1 076 368, US 6,278,236, and US 6,284,3936. Cathode materials are typically deposited by any suitable method such as evaporation, sputtering, or chemical vapor deposition. When needed, patterning can be achieved through many well known methods including, but not limited to, through-mask deposition, integral shadow masking as described in US 5,276,380 and EP 0 732 868, laser ablation, and selective chemical vapor deposition.

Hole-Injecting Layer (HIL)

A hole-injecting layer **105** may be provided between anode **103** and hole-transporting layer **107**. The hole-injecting layer can serve to improve the film

formation property of subsequent organic layers and to facilitate injection of holes into the hole-transporting layer **107**. Suitable materials for use in the hole-injecting layer **105** include, but are not limited to, porphyrinic compounds as described in US 4,720,432, plasma-deposited fluorocarbon polymers as described in US 6,208,075, and some aromatic amines, for example, MTDATA (4,4',4"-tris[(3-methylphenyl)phenylamino]triphenylamine). Alternative hole-injecting materials reportedly useful in organic EL devices are described in EP 0 891 121 A1 and EP 1 029 909 A1. A hole-injection layer is conveniently used in the present invention, and is desirably a plasma-deposited fluorocarbon polymer. The thickness of a hole-injection layer containing a plasma-deposited fluorocarbon polymer can be in the range of 0.2 nm to 15 nm and suitably in the range of 0.3 to 1.5 nm.

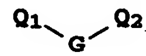
Hole-Transporting Layer (HTL)

In one embodiment, the hole-transporting layer **107** of the organic EL device contains at least one hole-transporting compound of Formula (1). The hole-transporting layer may contain additional materials, including additional hole-transporting materials. The hole-transporting layer, in turn, may contain more than one layer of hole-transporting materials. Examples of other useful hole-transporting materials include aromatic tertiary amine, where the latter is understood to be a compound containing at least one trivalent nitrogen atom that is bonded only to carbon atoms, at least one of which is a member of an aromatic ring. In one form the aromatic tertiary amine can be an arylamine, such as a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylamines are illustrated by Klupfel et al. US 3,180,730. Other suitable triarylamines substituted with one or more vinyl radicals and/or comprising at least one active hydrogen containing group are disclosed by Brantley et al US 3,567,450 and US 3,658,520.

A more preferred class of aromatic tertiary amines is that which includes at least two aromatic tertiary amine moieties as described in US

4,720,432 and US 5,061,569. Such compounds include those represented by structural formula (A).

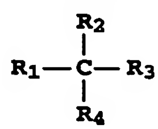
A



wherein Q_1 and Q_2 are independently selected aromatic tertiary amine moieties and G is a linking group such as an arylene, cycloalkylene, or alkylene group of a carbon to carbon bond. In one embodiment, at least one of Q_1 or Q_2 contains a polycyclic fused ring structure, e.g., a naphthalene. When G is an aryl group, it is conveniently a phenylene, biphenylene, or naphthalene moiety.

A useful class of triarylamines satisfying structural formula (A) and containing two triarylamine moieties is represented by structural formula (B):

B

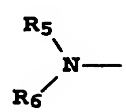


where

R_1 and R_2 each independently represents a hydrogen atom, an aryl group, or an alkyl group or R_1 and R_2 together represent the atoms completing a cycloalkyl group; and

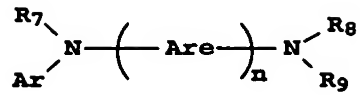
R_3 and R_4 each independently represents an aryl group, which is in turn substituted with a diaryl substituted amino group, as indicated by structural formula (C):

C



wherein R_5 and R_6 are independently selected aryl groups. In one embodiment, at least one of R_5 or R_6 contains a polycyclic fused ring structure, e.g., a naphthalene.

Another class of aromatic tertiary amines is the tetraaryldiamines. Desirable tetraaryldiamines include two diarylamino groups, such as indicated by formula (C), linked through an arylene group. Useful tetraaryldiamines include those represented by formula (D).

D 

wherein

each Ar is an independently selected arylene group, such as a phenylene or anthracene moiety,

n is an integer of from 1 to 4, and

Ar, R_7, R_8, and R_9 are independently selected aryl groups.

In a typical embodiment, at least one of Ar, R_7, R_8, and R_9 is a polycyclic fused ring structure, e.g., a naphthalene.

The various alkyl, alkylene, aryl, and arylene moieties of the foregoing structural formulae (A), (B), (C), (D), can each in turn be substituted. Typical substituents include alkyl groups, alkoxy groups, aryl groups, aryloxy groups, and halide such as fluoride, chloride, and bromide. The various alkyl and alkylene moieties typically contain from about 1 to 6 carbon atoms. The cycloalkyl moieties can contain from 3 to about 10 carbon atoms, but typically contain five, six, or seven ring carbon atoms--e.g.: cyclopentyl, cyclohexyl, and cycloheptyl ring structures. The aryl and arylene moieties are usually phenyl and phenylene moieties.

The hole-transporting layer can be formed of a single tertiary amine compound or a mixture of such compounds. Specifically, one may employ a triarylamine, such as a triarylamine satisfying the formula (B), in combination with a tetraaryldiamine, such as indicated by formula (D). Illustrative of useful aromatic tertiary amines are the following:

1,1-Bis(4-di-*p*-tolylaminophenyl)cyclohexane (TAPC)

1,1-Bis(4-di-*p*-tolylaminophenyl)-4-methylcyclohexane

1,1-Bis(4-di-*p*-tolylaminophenyl)-4-phenylcyclohexane

1,1-Bis(4-di-*p*-tolylaminophenyl)-3-phenylpropane (TAPPP)

N,N,N',N'-tetraphenyl-4,4'''-diamino-1,1':4',1'':4'',1'''-quaterphenyl

Bis(4-dimethylamino-2-methylphenyl)phenylmethane

1,4-bis[2-[4-[*N,N*-di(*p*-tolyl)amino]phenyl]vinyl]benzene (BDTAPVB)

N,N,N',N'-Tetra-*p*-tolyl-4,4'-diaminobiphenyl (TTB)

N,N,N',N'-Tetraphenyl-4,4'-diaminobiphenyl

N,N,N',N'-tetra-1-naphthyl-4,4'-diaminobiphenyl

N,N,N',N'-tetra-2-naphthyl-4,4'-diaminobiphenyl

N-Phenylcarbazole

4,4'-Bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB)

4,4'-Bis[*N*-(1-naphthyl)-*N*-(2-naphthyl)amino]biphenyl (TNB)

4,4'-Bis[*N*-(1-naphthyl)-*N*-phenylamino]*p*-terphenyl

4,4'-Bis[*N*-(2-naphthyl)-*N*-phenylamino]biphenyl

4,4'-Bis[*N*-(3-acenaphthenyl)-*N*-phenylamino]biphenyl

1,5-Bis[*N*-(1-naphthyl)-*N*-phenylamino]naphthalene

4,4'-Bis[*N*-(9-anthryl)-*N*-phenylamino]biphenyl

4,4'-Bis[*N*-(1-anthryl)-*N*-phenylamino]-*p*-terphenyl

4,4'-Bis[*N*-(2-phenanthryl)-*N*-phenylamino]biphenyl

4,4'-Bis[*N*-(8-fluoranthenyl)-*N*-phenylamino]biphenyl

4,4'-Bis[*N*-(2-pyrenyl)-*N*-phenylamino]biphenyl

4,4'-Bis[*N*-(2-naphthacenyl)-*N*-phenylamino]biphenyl

4,4'-Bis[*N*-(2-perylenyl)-*N*-phenylamino]biphenyl

4,4'-Bis[*N*-(1-coronenyl)-*N*-phenylamino]biphenyl

2,6-Bis(di-*p*-tolylamino)naphthalene

2,6-Bis[di-(1-naphthyl)amino]naphthalene

2,6-Bis[*N*-(1-naphthyl)-*N*-(2-naphthyl)amino]naphthalene

N,N,N',N'-Tetra(2-naphthyl)-4,4"-diamino-*p*-terphenyl

4,4'-Bis{*N*-phenyl-*N*-[4-(1-naphthyl)-phenyl]amino}biphenyl

2,6-Bis[*N,N*-di(2-naphthyl)amino]fluorene

4,4',4"-tris[(3-methylphenyl)phenylamino]triphenylamine (MTDATA)

4,4'-Bis[*N*-(3-methylphenyl)-*N*-phenylamino]biphenyl (TPD)

Another class of useful hole-transporting materials includes polycyclic aromatic compounds as described in EP 1 009 041. Tertiary aromatic amines with more than two amine groups may be used including oligomeric materials. In addition, polymeric hole-transporting materials can be used such as poly(*N*-vinylcarbazole) (PVK), polythiophenes, polypyrrole, polyaniline, and

copolymers such as poly(3,4-ethylenedioxythiophene) / poly(4-styrenesulfonate) also called PEDOT/PSS. It is also possible for the hole-transporting layer to comprise two or more sublayers of differing compositions, the composition of each sublayer being as described above. The thickness of the hole-transporting layer can be between 10 and about 500 nm and suitably between 50 and 300 nm.

Light-Emitting Layer (LEL)

As more fully described in U.S. Patent Nos. 4,769,292 and 5,935,721, the light-emitting layer (LEL) of the organic EL element includes a luminescent material where electroluminescence is produced as a result of electron-hole pair recombination. The light-emitting layer can be comprised of a single material, but more commonly consists of a host material doped with a guest emitting material or materials where light emission comes primarily from the emitting materials and can be of any color. The host materials in the light-emitting layer can be an electron-transporting material, as defined below, a hole-transporting material, as defined above, or another material or combination of materials that support hole-electron recombination. The light-emitting material can be fluorescent material or phosphorescent material. Fluorescent emitting materials are typically incorporated at 0.01 to 10 % by weight of the host material.

The host and emitting materials can be small non-polymeric molecules or polymeric materials such as polyfluorenes and polyvinylarylenes (e.g., poly(*p*-phenylenevinylene), PPV). In the case of polymers, small-molecule emitting materials can be molecularly dispersed into a polymeric host, or the emitting materials can be added by copolymerizing a minor constituent into a host polymer. Host materials may be mixed together in order to improve film formation, electrical properties, light emission efficiency, operating lifetime, or manufacturability. The host may comprise a material that has good hole-transporting properties and a material that has good electron-transporting properties.

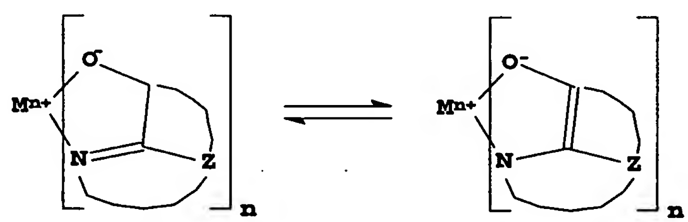
An important relationship for choosing a fluorescent material as a guest emitting material is a comparison of the excited singlet-state energies of the

host and the fluorescent material. It is highly desirable that the excited singlet-state energy of the fluorescent material be lower than that of the host material. The excited singlet-state energy is defined as the difference in energy between the emitting singlet state and the ground state. For non-emissive hosts, the lowest excited state of the same electronic spin as the ground state is considered the emitting state.

Host and emitting materials known to be of use include, but are not limited to, those disclosed in US 4,768,292, US 5,141,671, US 5,150,006, US 5,151,629, US 5,405,709, US 5,484,922, US 5,593,788, US 5,645,948, US 5,683,823, US 5,755,999, US 5,928,802, US 5,935,720, US 5,935,721, and US 6,020,078.

Metal complexes of 8-hydroxyquinoline and similar derivatives, also known as metal-chelated oxinoid compounds (Formula E), constitute one class of useful host compounds capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 500 nm, e.g., green, yellow, orange, and red.

E



wherein

M represents a metal;

n is an integer of from 1 to 4; and

Z independently in each occurrence represents the atoms completing a nucleus having at least two fused aromatic rings.

From the foregoing it is apparent that the metal can be monovalent, divalent, trivalent, or tetravalent metal. The metal can, for example, be an alkali metal, such as lithium, sodium, or potassium; an alkaline earth metal, such as magnesium or calcium; a trivalent metal, such aluminum or gallium, or another

metal such as zinc or zirconium. Generally any monovalent, divalent, trivalent, or tetravalent metal known to be a useful chelating metal can be employed.

Z completes a heterocyclic nucleus containing at least two fused aromatic rings, at least one of which is an azole or azine ring. Additional rings, including both aliphatic and aromatic rings, can be fused with the two required rings, if required. To avoid adding molecular bulk without improving on function the number of ring atoms is usually maintained at 18 or less.

Illustrative of useful chelated oxinoid compounds are the following:

CO-1: Aluminum trisoxine [alias, tris(8-quinolinolato)aluminum(III)]

CO-2: Magnesium bisoxine [alias, bis(8-quinolinolato)magnesium(II)]

CO-3: Bis[benzo{f}-8-quinolinolato]zinc (II)

CO-4: Bis(2-methyl-8-quinolinolato)aluminum(III)-μ-oxo-bis(2-methyl-8-quinolinolato) aluminum(III)

CO-5: Indium trisoxine [alias, tris(8-quinolinolato)indium]

CO-6: Aluminum tris(5-methyloxine) [alias, tris(5-methyl-8-quinolinolato) aluminum(III)]

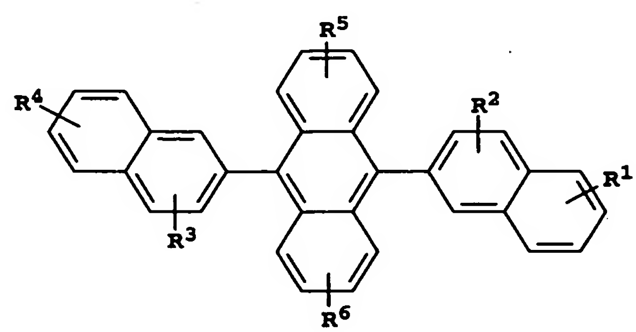
CO-7: Lithium oxine [alias, (8-quinolinolato)lithium(I)]

CO-8: Gallium oxine [alias, tris(8-quinolinolato)gallium(III)]

CO-9: Zirconium oxine [alias, tetra(8-quinolinolato)zirconium(IV)]

Derivatives of 9,10-di-(2-naphthyl)anthracene (Formula F) constitute one class of useful host materials capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 400 nm, e.g., blue, green, yellow, orange or red.

F



wherein: R^1, R^2, R^3, R^4, R^5, and R^6 represent one or more substituents on each ring where each substituent is individually selected from the following groups:

Group 1: hydrogen, or alkyl of from 1 to 24 carbon atoms;

Group 2: aryl or substituted aryl of from 5 to 20 carbon atoms;

Group 3: carbon atoms from 4 to 24 necessary to complete a fused aromatic ring of anthracenyl; pyrenyl, or perylenyl;

Group 4: heteroaryl or substituted heteroaryl of from 5 to 24 carbon atoms as necessary to complete a fused heteroaromatic ring of furyl, thienyl, pyridyl, quinolinyl or other heterocyclic systems;

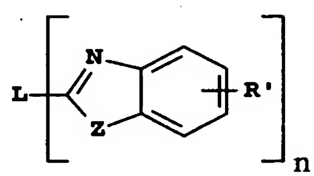
Group 5: alkoxylamino, alkylamino, or arylamino of from 1 to 24 carbon atoms; and

Group 6: fluorine, chlorine, bromine or cyano.

Illustrative examples include 9,10-di-(2-naphthyl)anthracene and 2-*t*-butyl-9,10-di-(2-naphthyl)anthracene. Other anthracene derivatives can be useful as a host in the LEL, including derivatives of 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene.

Benzazole derivatives (Formula G) constitute another class of useful host materials capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 400 nm, e.g., blue, green, yellow, orange or red.

G



wherein:

n is an integer of 3 to 8;

Z is O, NR or S; and

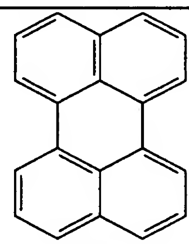
R and R' are individually hydrogen; alkyl of from 1 to 24 carbon atoms, for example, propyl, t-butyl, heptyl, and the like; aryl or hetero-atom substituted aryl of from 5 to 20 carbon atoms for example phenyl and naphthyl, furyl, thienyl,

pyridyl, quinolinyl and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring; and

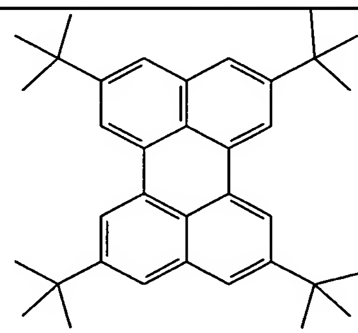
L is a linkage unit consisting of alkyl, aryl, substituted alkyl, or substituted aryl, which connects the multiple benzazoles together. L may be either conjugated with the multiple benzazoles or not in conjugation with them. An example of a useful benzazole is 2,2',2"-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole].

Styrylarylene derivatives as described in U.S. Patent 5,121,029 and JP 08333569 are also useful hosts for blue emission. For example, 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene and 4,4'-bis(2,2-diphenylethenyl)-1,1'-biphenyl (DPVBi) are useful hosts for blue emission.

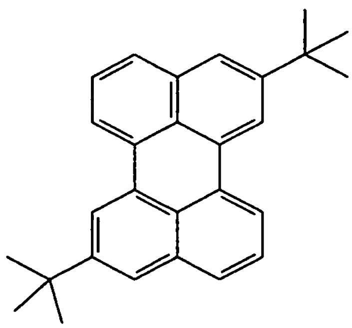
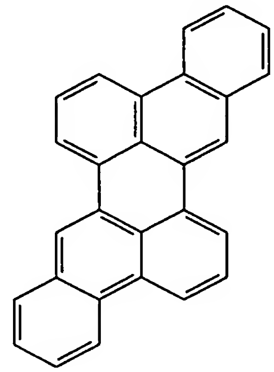
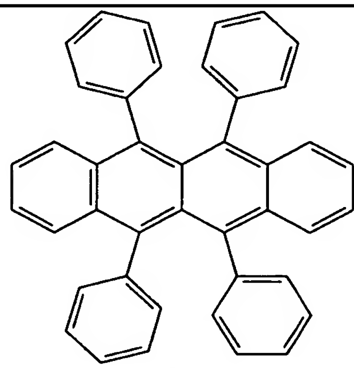
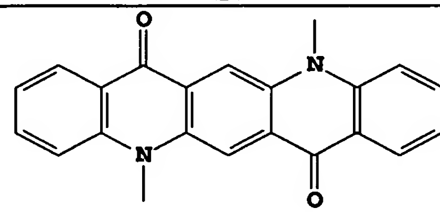
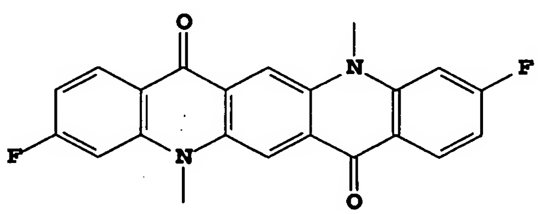
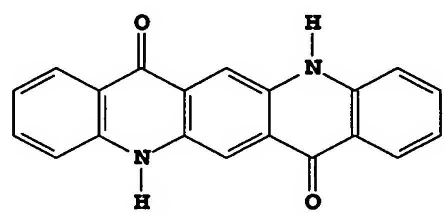
Useful fluorescent emitting materials include, but are not limited to, derivatives of anthracene, tetracene, xanthene, perylene, rubrene, coumarin, rhodamine, and quinacridone, dicyanomethylenepyran compounds, thiopyran compounds, polymethine compounds, pyrylium and thiapyrylium compounds, fluorene derivatives, periflanthene derivatives, indenoperylene derivatives, bis(azinyl)amine boron compounds, bis(azinyl)methane compounds, and carbostyryl compounds. Illustrative examples of useful materials include, but are not limited to, the following:

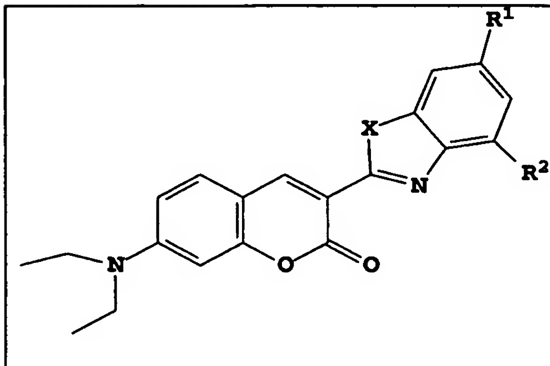


L1

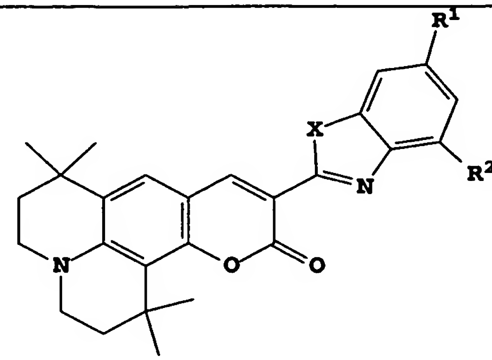


L2

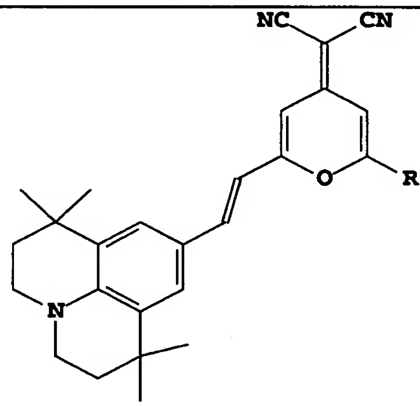
 L3	 L4
 L5	 L6
 L7	 L8



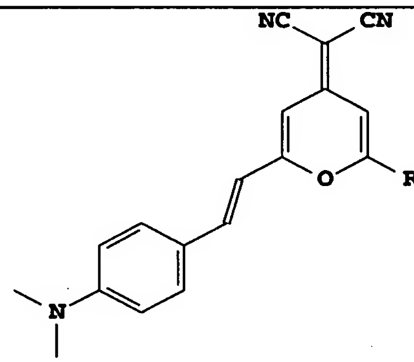
	X	R1	R2
L9	O	H	H
L10	O	H	Methyl
L11	O	Methyl	H
L12	O	Methyl	Methyl
L13	O	H	*t*-butyl
L14	O	*t*-butyl	H
L15	O	*t*-butyl	*t*-butyl
L16	S	H	H
L17	S	H	Methyl
L18	S	Methyl	H
L19	S	Methyl	Methyl
L20	S	H	*t*-butyl
L21	S	*t*-butyl	H
L22	S	*t*-butyl	*t*-butyl



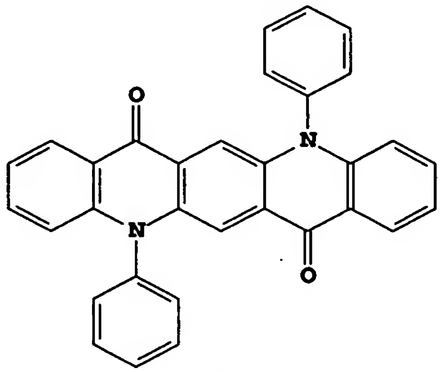
	X	R1	R2
L23	O	H	H
L24	O	H	Methyl
L25	O	Methyl	H
L26	O	Methyl	Methyl
L27	O	H	*t*-butyl
L28	O	*t*-butyl	H
L29	O	*t*-butyl	*t*-butyl
L30	S	H	H
L31	S	H	Methyl
L32	S	Methyl	H
L33	S	Methyl	Methyl
L34	S	H	*t*-butyl
L35	S	*t*-butyl	H
L36	S	*t*-butyl	*t*-butyl



	R
L37	phenyl
L38	methyl
L39	*t*-butyl
L40	mesityl



	R
L41	phenyl
L42	methyl
L43	*t*-butyl
L44	mesityl



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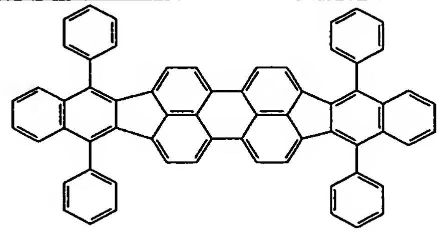

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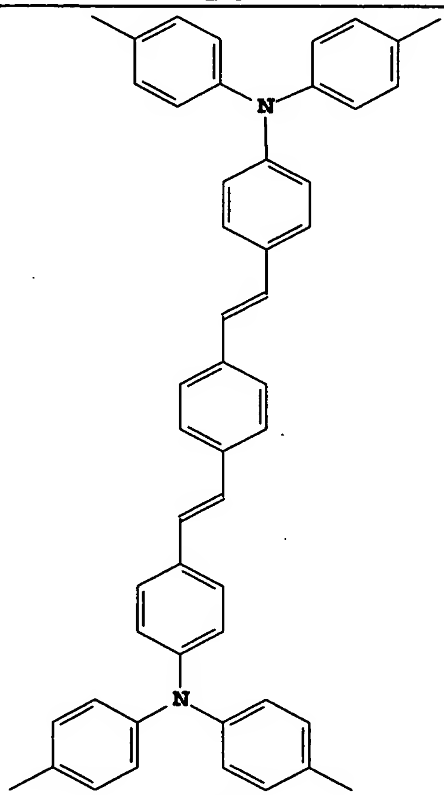

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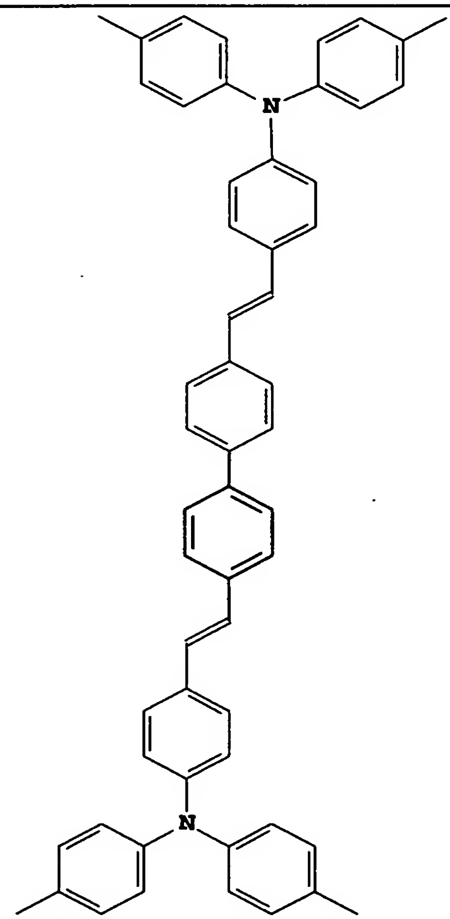

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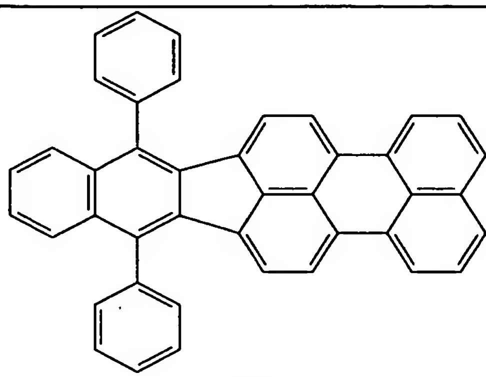
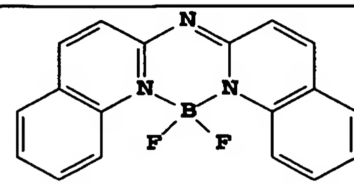
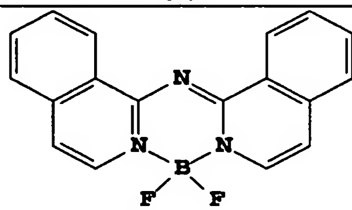
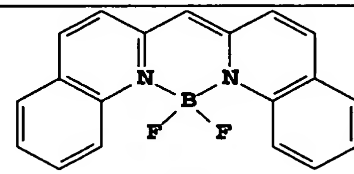
 L49	 L50
 L51	 L52

In addition to, or in place of, fluorescent light-emitting materials, light-emitting phosphorescent materials may be used in the EL device. For convenience, the phosphorescent complex guest material may be referred to herein as a phosphorescent material. The phosphorescent material typically includes one or more ligands, for example monoanionic ligands that can be coordinated to a metal through an sp^2 carbon and a heteroatom. Conveniently, the ligand can be phenylpyridine (ppy) or derivatives or analogs thereof. Examples of some useful phosphorescent organometallic materials include tris(2-phenylpyridinato-$N,C^{2'}$)iridium(III), bis(2-phenylpyridinato-N,C^{2})iridium(III)(acetylacetonate), and bis(2-phenylpyridinato-$N,C^{2'}$)platinum(II). Usefully, many phosphorescent organometallic materials emit in the green region of the spectrum, that is, with a maximum emission in the range of 510 to 570 nm.

Phosphorescent materials may be used singly or in combinations other phosphorescent materials, either in the same or different layers. Phosphorescent materials and suitable hosts are described in WO 00/57676, WO 00/70655, WO 01/41512 A1, WO 02/15645 A1, US 2003/0017361 A1, WO 01/93642 A1, WO 01/39234 A2, US 6,458,475 B1, WO 02/071813 A1, US 6,573,651 B2, US 2002/0197511 A1, WO 02/074015 A2, US 6,451,455 B1, US

2003/ 0072964 A1, US 2003 / 0068528 A1, US 6,413,656 B1, US 6,515,298 B2, US 6,451,415 B1, US 6,097,147, US 2003/0124381 A1, US 2003/0059646 A1, US 2003/0054198 A1, EP 1 239 526 A2, EP 1 238 981 A2, EP 1 244 155 A2, US 2002/0100906 A1, US 2003 / 0068526 A1, US 2003/0068535 A1, JP 2003073387A, JP 2003 073388A, US 2003/0141809 A1, US 2003/0040627 A1, JP 2003059667A, JP 2003073665A, and US 2002/0121638 A1.

The emission wavelengths of cyclometallated Ir(III) complexes of the type IrL_3 and IrL_2L', such as the green-emitting *fac*-tris(2-phenylpyridinato-$N,C^{2'}$)iridium(III) and bis(2-phenylpyridinato-$N,C^{2'}$)iridium(III)(acetylacetonate) may be shifted by substitution of electron donating or withdrawing groups at appropriate positions on the cyclometallating ligand L, or by choice of different heterocycles for the cyclometallating ligand L. The emission wavelengths may also be shifted by choice of the ancillary ligand L'. Examples of red emitters are the bis(2-(2'-benzothienyl)pyridinato-$N,C^{3'}$)iridium(III)(acetylacetonate) and tris(2-phenylisoquinolinato-N,C)iridium(III). A blue-emitting example is bis(2-(4,6-difluorophenyl)-pyridinato-$N,C^{2'}$)iridium(III)(picolinate).

Red electrophosphorescence has been reported, using bis(2-(2'-benzo[4,5-a]thienyl)pyridinato-N, C^3) iridium (acetylacetonate) [$Btp_2Ir(acac)$] as the phosphorescent material (C. Adachi, S. Lamansky, M. A. Baldo, R. C. Kwong, M. E. Thompson, and S. R. Forrest, *App. Phys. Lett.*, **78**, 1622-1624 (2001)).

Other important phosphorescent materials include cyclometallated Pt(II) complexes such as cis-bis(2-phenylpyridinato-$N,C^{2'}$)platinum(II), cis-bis(2-(2'-thienyl)pyridinato-$N,C^{3'}$) platinum(II), cis-bis(2-(2'-thienyl)quinolinato-$N,C^{5'}$) platinum(II), or (2-(4,6-difluorophenyl)pyridinato-$N,C^{2'}$) platinum (II) (acetylacetonate). Pt (II) porphyrin complexes such as 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphine platinum(II) are also useful phosphorescent materials.

Still other examples of useful phosphorescent materials include coordination complexes of the trivalent lanthanides such as Tb^{3+} and Eu^{3+} (J. Kido et al., *Appl. Phys. Lett.*, **65**, 2124 (1994)).

Suitable host materials for phosphorescent materials should be selected so that transfer of a triplet exciton can occur efficiently from the host material to the phosphorescent material but cannot occur efficiently from the phosphorescent material to the host material. Therefore, it is highly desirable that the triplet energy of the phosphorescent material be lower than the triplet energy of the host. Generally speaking, a large triplet energy implies a large optical bandgap. However, the band gap of the host should not be chosen so large as to cause an unacceptable barrier to injection of charge carriers into the light-emitting layer and an unacceptable increase in the drive voltage of the OLED. Suitable host materials are described in WO 00/70655 A2; 01/39234 A2; 01/ 93642 A1; 02/074015 A2; 02/15645 A1, and US 20020117662. Suitable hosts include certain aryl amines, triazoles, indoles and carbazole compounds. Examples of desirable hosts are 4,4'-*N,N'*-dicarbazole-biphenyl, otherwise known as 4,4'-bis(carbazol-9-yl)biphenyl or CBP; 4,4'-*N,N'*-dicarbazole-2,2'-dimethyl-biphenyl, otherwise known as 2,2'-dimethyl-4,4'-bis(carbazol-9-yl)biphenyl or CDBP; 1,3-bis(*N,N'*-dicarbazole)benzene, otherwise known as 1,3-bis(carbazol-9-yl)benzene, and poly(*N*-vinylcarbazole), including their derivatives.

Desirable host materials are capable of forming a continuous film.

Hole-Blocking Layer (HBL)

In addition to suitable hosts, an OLED device employing a phosphorescent material often requires at least one hole-blocking layer placed between the electron-transporting layer **111** and the light-emitting layer **109** to help confine the excitons and recombination events to the light-emitting layer comprising the host and phosphorescent material. In this case, there should be an energy barrier for hole migration from the host into the hole-blocking layer, while electrons should pass readily from the hole-blocking layer into the light-emitting layer comprising a host and a phosphorescent material. The first requirement entails that the ionization potential of the hole-blocking layer be larger than that of the light-emitting layer **109**, desirably by 0.2 eV or more. The second requirement entails that the electron affinity of the hole-blocking layer not greatly exceed that

of the light-emitting layer **109**, and desirably be either less than that of light-emitting layer or not exceed that of the light-emitting layer by more than about 0.2 eV.

When used with an electron-transporting layer whose characteristic luminescence is green, such as an Alq-containing electron-transporting layer as described below, the requirements concerning the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the material of the hole-blocking layer frequently result in a characteristic luminescence of the hole-blocking layer at shorter wavelengths than that of the electron-transporting layer, such as blue, violet, or ultraviolet luminescence. Thus, it is desirable that the characteristic luminescence of the material of a hole-blocking layer be blue, violet, or ultraviolet. It is further desirable, but not absolutely required, that the triplet energy of the hole-blocking material be greater than that of the phosphorescent material. Suitable hole-blocking materials are described in WO 00/70655A2 and WO 01/93642 A1. Two examples of useful hole-blocking materials are bathocuproine (BCP) and bis(2-methyl-8-quinolinolato)(4-phenylphenolato)aluminum(III) (BAlq). The characteristic luminescence of BCP is in the ultraviolet, and that of BAlq is blue. Metal complexes other than BAlq are also known to block holes and excitons as described in US 20030068528. In addition, US 20030175553 A1 describes the use of *fac*-tris(1-phenylpyrazolato-$N,C^{2'}$)iridium(III) (Irppz) for this purpose.

When a hole-blocking layer is used, its thickness can be between 2 and 100 nm and suitably between 5 and 10 nm.

Electron-Transporting Layer (ETL)

Desirable thin film-forming materials for use in forming the electron-transporting layer **111** of the organic EL devices of this invention are metal-chelated oxinoid compounds, including chelates of oxine itself (also commonly referred to as 8-quinolinol or 8-hydroxyquinoline). Such compounds help to inject and transport electrons, exhibit high levels of performance, and are readily fabricated in the form of thin films. Exemplary of contemplated oxinoid compounds are those satisfying structural formula (E), previously described.

Other electron-transporting materials suitable for use in the electron-transporting layer **111** include various butadiene derivatives as disclosed in US 4,356,429 and various heterocyclic optical brighteners as described in US 4,539,507. Benzazoles satisfying structural formula (G) are also useful electron transporting materials. Triazines are also known to be useful as electron transporting materials.

If both a hole-blocking layer and an electron-transporting layer **111** are used, electrons should pass readily from the electron-transporting layer **111** into the hole-blocking layer. Therefore, the electron affinity of the electron-transporting layer **111** should not greatly exceed that of the hole-blocking layer. Desirably, the electron affinity of the electron-transporting layer should be less than that of the hole-blocking layer or not exceed it by more than about 0.2 eV.

If an electron-transporting layer is used, its thickness may be between 2 and 100 nm and suitably between 5 and 20 nm.

Other Useful Organic Layers and Device Architecture

In some instances, layers **109** through **111** can optionally be collapsed into a single layer that serves the function of supporting both light emission and electron transportation. The hole-blocking layer, when present, and layer **111** may also be collapsed into a single layer that functions to block holes or excitons, and supports electron transport. It also known in the art that emitting materials may be included in the hole-transporting layer **107**. In that case, the hole-transporting material may serve as a host. Multiple materials may be added to one or more layers in order to create a white-emitting OLED, for example, by combining blue- and yellow-emitting materials, cyan- and red-emitting materials, or red-, green-, and blue-emitting materials. White-emitting devices are described, for example, in EP 1 187 235, US 20020025419, EP 1 182 244, US 5,683,823, US 5,503,910, US 5,405,709, and US 5,283,182 and can be equipped with a suitable filter arrangement to produce a color emission.

This invention may be used in so-called stacked device architecture, for example, as taught in US 5,703,436 and US 6,337,492.

Deposition of Organic Layers

The organic materials mentioned above are suitably deposited by any means suitable for the form of the organic materials. In the case of small molecules, they are conveniently deposited through sublimation or evaporation, but can be deposited by other means such as coating from a solvent together with an optional binder to improve film formation. If the material is a polymer, solvent deposition is usually preferred. The material to be deposited by sublimation or evaporation can be vaporized from a sublimator "boat" often comprised of a tantalum material, e.g., as described in US 6,237,529, or can be first coated onto a donor sheet and then sublimed in closer proximity to the substrate. Layers with a mixture of materials can utilize separate sublimator boats or the materials can be pre-mixed and coated from a single boat or donor sheet. Patterned deposition can be achieved using shadow masks, integral shadow masks (US 5,294,870), spatially-defined thermal dye transfer from a donor sheet (US 5,688,551, US 5,851,709 and US 6,066,357) or an inkjet method (US 6,066,357).

Encapsulation

Most OLED devices are sensitive to moisture or oxygen, or both, so they are commonly sealed in an inert atmosphere such as nitrogen or argon, along with a desiccant such as alumina, bauxite, calcium sulfate, clays, silica gel, zeolites, alkaline metal oxides, alkaline earth metal oxides, sulfates, or metal halides and perchlorates. Methods for encapsulation and desiccation include, but are not limited to, those described in U.S. Patent No. 6,226,890. In addition, barrier layers such as SiO_x, Teflon, and alternating inorganic/polymeric layers are known in the art for encapsulation. Any of these methods of sealing or encapsulation and desiccation can be used with the EL devices constructed according to the present invention.

Optical Optimization

OLED devices of this invention can employ various well-known optical effects in order to enhance their emissive properties if desired. This includes optimizing layer thicknesses to yield maximum light transmission, providing dielectric mirror structures, replacing reflective electrodes with light-

absorbing electrodes, providing anti-glare or anti-reflection coatings over the display, providing a polarizing medium over the display, or providing colored, neutral density, or color-conversion filters over the display. Filters, polarizers, and anti-glare or anti-reflection coatings may be specifically provided over the EL device or as part of the EL device.

Embodiments of the invention may provide advantageous features such as higher luminous yield, lower drive voltage, and higher power efficiency, or reduced sublimation temperatures, or higher Tg materials. Embodiments of devices useful in the invention can provide a wide range of hues including those useful in the emission of white light (directly or through filters to provide multicolor displays). Embodiments of the invention can also provide an area lighting device.

The invention and its advantages can be better appreciated by the following examples

Synthesis Example 1: Preparation of Inv-7.

N,N,N'-Triphenyl-1,5-diaminonaphthalene was prepared by combining 1,5-Diaminonaphthalene (16.0 g, 0.101 mol) with bromobenzene (47.1 g, 0.300 mol), palladium diacetate (1.2 g, 0.004 mol), tri-*t*-butylphosphine (4 mL), sodium t-butoxide (24.0g, 0.26 mol), and xylene (400 mL). The mixture was heated at 140 °C with magnetic stirring under a nitrogen atmosphere. After 15 h, an additional amount of palladium diacetate (0.100 g, 0.0004 mol) was added. After heating for another 6 h, more palladium diacetate (0.100 g, 0.0004 mol) was added. After heating for another 15 h the heat was removed. After cooling to room temperature, the solid present was filtered off and the filtrate was purified by column chromatography. This afforded 6.0 g (15% yield) of *N,N,N'*-triphenyl-1,5-diaminonaphthalene.

1,5-dibromo-2,6-di-*t*-butylnapthalene was prepared from 2,6-Di-*t*-butylnaphthalene (see R. Harvey, J. Pataki, C. Cortez, P. Di Raddo, C. Yang, *J. Org. Chem.*, **56**, 1210 (1991)). 2,6-Di-*t*-butylnaphthalene (5.0g, 20.8 mmol) and aluminum chloride (50 mg) and 50 mL of methylene chloride were combined with

magnetic stirring in a 50 mL round-bottomed-flask with an addition funnel and nitrogen inlet. Bromine (7.2 g, 45.2 mmol) in 15 mL of methylene chloride was added over 15 min. The reaction mixture was stirred for 2 h and an additional 1 mL of bromine in 5 mL of methylene chloride was added and the mixture was stirred for 18 h. An additional 0.5 mL of bromine was then added and the mixture was stirred for 6 h. The reaction mixture was extracted with water and then with 5% sodium hydroxide solution. The methylene chloride solution was dried with magnesium sulfate and evaporated under reduced pressure. The solid obtained was slurried with ethanol and then collected, to afford 3.6g of product, *N,N,N'*-triphenyl-1,5-diaminonaphthalene (43%), mp 200-203 °C.

Compound Inv-7 was prepared by combining *N,N,N'*-triphenyl-1,5-diaminonaphthalene (1.55 g, 2.0 mmol), 1,5-dibromo-2,6-di-*t*-butylnapthalene (0.8 g, 2 mmol), palladium diacetate (110 mg, 0.4 mmol), tri-*t*-butylphosphine (6 drops), sodium t-butoxide (0.5 g, 5.2 mmol), and toluene (50 mL) and heating to 105 - 110 °C with magnetic stirring under a nitrogen atmosphere. After 3 h the heat was removed and the reaction mixture was vacuum filtered. The filtrate was evaporated to a solid. The solid was slurried with EtOH and collected. The crude solid was combined with 50 mL of methylene chloride with stirring for 20 min. The solid was collected and washed with ethyl acetate and dried under vacuum to afford 2.0 g of crude product. This material was sublimed at 345 – 350 °C at 0.9 Torr and then sublimed again at 327 – 335 °C and 0.6 Torr to afford 1.2 g of product, Inv-7, (60% yield), mass spectrum m/e: 1008.5, 1009.5.

Synthesis Example 2: Preparation of Inv-1

Compound Inv-1 was prepared by combining *N-α*-naphthyl, *N-β*-naphthylamine (2.0 g, 7.4 mmol), 1,5-dibromo-2,6-di-*t*-butylnaphthalene (1.5 g, 3.77 mmol) palladium diacetate (0.110 g, 0.5 mmol), tri-*t*-butylphosphine (ca. 0.4 mL), sodium *t*-butoxide (0.85 g, 9.2 mmol), and toluene (40 mL) in a 100 mL round-bottomed-flask under nitrogen and with magnetic stirring. The reaction mixture was heated at reflux and after 1 h, 0.4 mL of tri-*t*-butylphosphine was added and heating was continued, after a total of 4 h, 150 mg of palladium

diacetate was added and the reaction mixture was heated for 16 h. Palladium diacetate (150 mg) was added and heating was continued for 3.5 h. The heat was removed and the reaction mixture was stirred for 60 h. Palladium diacetate (50 mg) was then added and the reaction mixture was heated at reflux for 4 h. The heat was removed and, after cooling, solid material was filtered off. The filtrate was evaporated and the solid obtained was dissolved in the minimum amount of ethyl acetate and then diluted with 75 mL of ethanol; the solid that precipitated was collected (2.5 g). The solid was slurried with 50 mL of ethyl acetate, and then collected (2.0 g). This material was sublimed twice at 260 - 265 °C and 0.6 torr. Sublimation afforded Inv-1, 1.2 g (21 % yield).

Device Example 1

An EL device (Sample 1) satisfying the requirements of the invention was constructed in the following manner:

1. A glass substrate coated with an 85 nm layer of indium-tin oxide (ITO) as the anode was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water, degreased in toluene vapor and exposed to oxygen plasma for about 1 min.
2. Over the ITO was deposited a 1 nm fluorocarbon (CFx) hole-injecting layer (HIL) by plasma-assisted deposition of CHF_3.
3. A first hole-transporting layer (HTL)of Inv-1 having a thickness of 75 nm was then evaporated from a tantalum boat.
4. A 37.5 nm light-emitting layer (LEL) of tris(8-quinolinolato)aluminum (III) (AlQ_3) and dopant DPQ (0.6 wt%, see structure below) were then deposited onto the hole-transporting layer. These materials were also evaporated from tantalum boats.

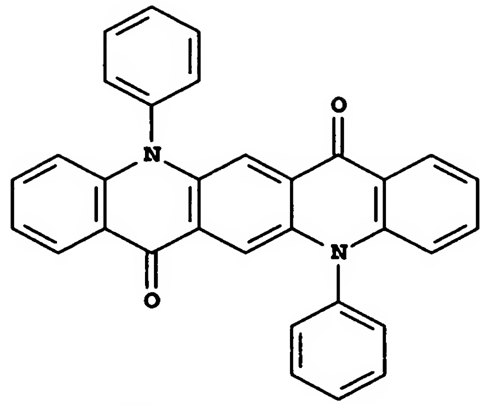
5. A 37.5 nm electron-transporting layer (ETL) of tris(8-quinolinolato)aluminum (III) (AlQ_3) was then deposited onto the light-emitting layer. This material was also evaporated from a tantalum boat.

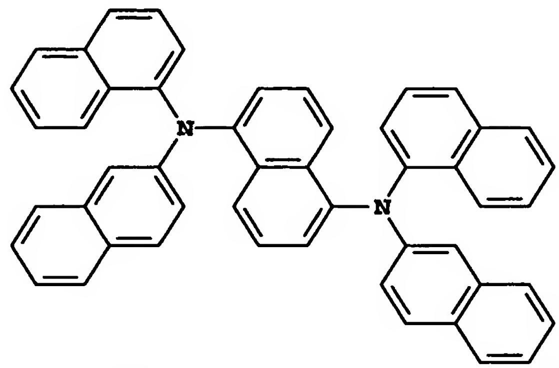
6. On top of the AlQ_3 layer was deposited a 220 nm cathode formed of a 10:1 volume ratio of Mg and Ag.

The above sequence completed the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.

A comparative device, Sample 2, was prepared in the same manner as Sample 1, except in the HTL layer compound Inv-1 was replaced with comparison compound Com-1. Device Sample 3 was prepared in the same manner as Sample 1, except in the HTL layer compound Inv-1 was replaced with 4,4'-bis[*N*-(1-naphthyl)-*N*-(2-naphthyl)amino]biphenyl (TNB). Device Sample 4 was prepared in a manner similar to Sample 1, except the HTL was formed by depositing two layers, a first layer (HTL-1) of 70.0 nm of Compound Inv-1 followed by depositing a second layer (HTL-2) of 5.0 nm of TNB. The total HTL layer thickness remained at 75.0 nm. Device Sample 5 was prepared in the same manner as Sample 4, except Inv-1 was replaced with Com-1. Device Sample 6 was prepared in a manner similar to Sample 4, except a first layer (HTL-1) of 55.0 nm of Compound Inv-1 followed by depositing a second layer (HTL-2) of 20.0 nm of TNB. Device Sample 6 was prepared in the same manner as Sample 5, except Inv-1 was replaced with Com-1.

The cells thus formed were tested for efficiency in the form of luminance (cd/m^2) at a current density of 20 mA/cm^2. The devices were also tested by operating them at a current density of 20 mA/cm^2 for 300 hours at room temperature. The initial and final luminance of the devices was recorded. Results are listed in Table 1.

DPQ 

Com-1 

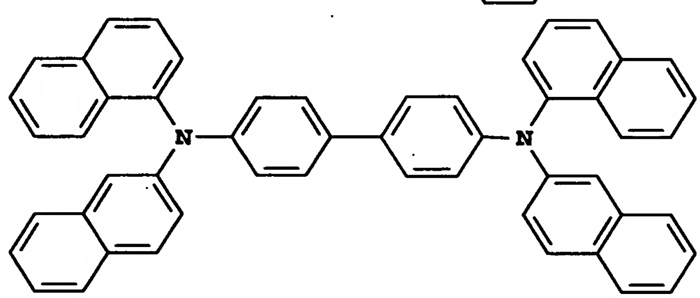
TNB 

TABLE 1. EVALUATION RESULTS FOR EL DEVICES

Sample	Example	HTL-1 Material	HTL-1 nm	HTL-2 Material	HTL-2 nm	Luminance (cd/m^2) Initial	Luminance (cd/m^2) Final
1	Inventive	Inv-1	75.0	-	-	2501	2125
2	Comparative	Com-1	75.0	-	-	2169	1888
3	Comparative	TNB	75.0	-	-	2112	1858
4	Inventive	Inv-1	70.0	TNB	0.5	2539	2152
5	Comparative	Com-1	70.0	TNB	0.5	1989	1806
6	Inventive	Inv-1	55.0	TNB	20.0	2491	2180
7	Comparative	Com-1	55.0	TNB	20.0	2339	2126

As can be seen from Table 1, the tested EL devices incorporating the invention hole-transporting material demonstrates a superior luminance

relative to the comparative devices containing either Com-1 or TNB even after operating for 300 hours (Samples 1-3). When the invention hole-transporting material is used in combination with a conventional hole-transporting material such as TNB (Sample 4 and Sample 6) luminance output is improved even after operating for 300 hours relative to a device using only TNB (Sample 3) or a device using Com-1 and TNB (Sample 5 and Sample 7).

Device Example 2

Device Sample 7 was prepared in the same manner as Sample 1, except hole-transporting material Inv-7 was used in place of Inv-1. Sample 8 was prepared in the same manner as Sample 6, except the HTL was formed by depositing a layer of 55.0 nm of Compound Inv-7 followed by depositing a layer of 20.0 nm of TNB. Sample 9 was prepared in the same manner as sample 8 except compound Inv-7 was replaced with TNB.

The cells thus formed were tested for efficiency in the form of luminance (cd/m^2) at a current density of 20 mA/cm^2. The devices were also tested by operating them at a current density of 20 mA/cm^2 for 300 hours at a temperature of 70° C. The initial and final luminance of the devices was recorded. Results are listed in Table 2.

Table 2. Evaluation Results for EL devices

		HTL-1		HTL-2		Luminance (cd/M^2)	
Sample	Example	Material	nm	Material	nm	Initial	Final
7	Inventive	Inv-7	75.0	-	-	1811	1318
8	Inventive	Inv-7	55.0	TNB	20.0	1877	1267
9	Comparison	TNB	75.0	-	-	1453	1093

As can be seen from Table 2, the tested EL devices incorporating the invention hole-transporting material or a combination of the invention hole-transporting material and TNB demonstrate a superior luminance relative to the comparative devices containing only TNB even after operating for 300 hours at 70°C.

The entire contents of the patents and other publications referred to in this specification are incorporated herein by reference. The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

PARTS LIST

101 Substrate

103 Anode

105 Hole-Injecting layer (HIL)

107 Hole-Transporting layer (HTL)

109 Light-Emitting layer (LEL)

111 Electron-Transporting layer (ETL)

113 Cathode